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Phase I Final Report

Agency: BMDO

Contract No. F49620-95-C-0071

Development of a Low-Loss Electro-Optic Polymer at 980 nm

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1. IDENTIFICATION AND SIGNIFICANCE OF THE PROBLEM AND OPPORTUNITY

Liquid crystal displays (LCDs) presently dominate the flat panel display market. However, as a mature technology, cost and performance specifications of LCDs are expected to improve only incrementally beyond current levels. The primary limitations of this technology are its lack of scalability, low brightness, low efficiency, and limited viewing angle. Most applications would benefit from better performance in some or all of these areas; and many, including important DoD applications, require it. Many DoD applications also need greater ruggedness; thinner, lighter packaging; mechanical flexibility and even transparency, provided that these attributes are not met at the expense of basic requirements such as resolution, efficiency and cost.

Deacon Research (DR) has developed a new concept for flat panel displays that promises to significantly exceed the LCD performance in each of the above areas. Fabricated in the form of thin polymer films with driver circuitry attached, it features scalability to large formats, high brightness, high efficiency (i.e., low power consumption), and large viewing angle, without sacrificing resolution or cost. Our concept, called the Polymer Switched Matrix™ (PSM™), is based on years of enabling technology development by DR. With PSM displays, infrared laser radiation is guided to the pixel locations of the display in a thin polymer film on the surface of a plastic substrate, using an array of electro-optic (EO) waveguide switches. The IR radiation is converted to visible light at each location using up-conversion phosphors. Full color displays can be designed with a color gamut equivalent to or better than current LCDs. Importantly, the integrated structures which make this possible can be fabricated using microlithographic techniques that have been well developed in the semiconductor and LCD industries. Moreover, the use of polymer-based materials allows the display to be extremely rugged and shock resistant, to be mechanically flexible (i.e., it can be used in curved display architectures), to be paper-thin and very light weight, and to be transparent enough for "see through" display applications. No other display technology, currently available or under development, can match the projected suite of performance characteristics of the Polymer Switched Matrix display.

Electro-optic polymers also show enormous potential for active thin film devices in other integrated optics and optoelectronic applications. Researchers at several institutions have demonstrated polymeric optical devices, including optical rail-taps, Mach-Zehnder interferometers, optical switches, and various telecommunications-related (i.e., high speed, large bandwidth) applications. Most of these uses involve structures and materials that are optimized for 1.3 micron light. DR team member USC has demonstrated highly efficient devices at 1.3 microns using electro-optic polymers that are simultaneously highly nonlinear, have excellent thermal and temporal stability, and low waveguide loss. However, these materials have higher losses at 800-1000 nm and, therefore, are not practical for PSM display applications.

The goal of Phase I was to develop high- $\mu\beta$ chromophores with low absorption loss and high bulk EO nonlinearity at 980 nm. Such material(s) would be ideal for the PSM display. Toward this end, the Phase I work focused on second-order optical nonlinearities in dipolar chromophores of the general form (electron donor)-(π -bridge)-(electron acceptor). Six different methods of "engineering" such material were explored. Two of the methods studied focused on improving the electron donor functional group; two focused on improving the π -bridge

architecture; and two focused on improving the electron acceptor functional group. Four showed sufficient promise to warrant further consideration in Phase II.

Phase I also attempted to incorporate one particularly promising chromophore into a polymer host but less-than-expected bulk nonlinearities were encountered due to what was ultimately determined to be centrosymmetric crystallization. This phenomenon was successfully modeled with London theory and a quantitative comparison between theory and experiments performed. From the quality of these results Phase II solutions to the observed problem can be postulated with good confidence.

Lastly, the Phase I work plan was expanded to include measurements of waveguide loss of several high- $\mu\beta$ chromophores in a poled guest-host polymer material system. Intrinsic measurements of the absorption spectrum at 980 nm indicates that the λ_{max} can be red shifted to longer than 550 nm (as in the case of isoxazolone) before the tail of the chromophore absorption starts to affect transmission losses at 980 nm. This is a particularly significant result; since it expands the parameter space in which the nonlinearity/transparency tradeoff can be optimized during Phase II.

Based on these, we believe that the feasibility of developing a protocol for systematically designing blue-shifted chromophores with high bulk nonlinearities has been demonstrated. Moreover, by exploring not one, but several, different and promising materials systems, we have laid a solid theoretical and experimental foundation for the Phase II work, greatly improving the chances of technical and commercial success.

1.1 EO Polymer Requirements

The EO polymer may be spun onto any flat substrate (such as glass, polyamide, etc.) prior to processing. It therefore has a potential cost advantage. Our projected cost is \$0.15 per in². However, despite the fact that electro-optic polymers have been under development for years, it was not until recently that a sufficiently long lifetime has been demonstrated for a high nonlinearity material. This advance was achieved at the University of Southern California by Prof. Larry Dalton's group, who have developed a new class of double-ended cross-linked polymers. These materials retain over 80% of their nonlinearity when subjected to elevated temperatures of 100°C for 1000 hours, which scales to fully adequate lifetimes at temperatures for the display application. Furthermore, they exhibit an electro-optic coefficient equal to lithium niobate, the "gold standard" for EO materials. All of these demonstrations have been performed at 1.3 μm . These materials need to be optimized for operation at 980 nm to be useful for PSM display purposes. Under this Phase I program, we started the development of low-loss, high-performance EO polymer materials that are transparent at the operating wavelength 980 nm by combination of designing and synthesizing novel blue-shifted, highly nonlinear chromophores, and incorporating these chromophores into thermally stable polymeric lattices. A list of the important material specifications for display applications is given in Table 1.

Second-order optical nonlinearities have largely focused upon dipolar chromophores of the form (electron donor)-(π -electron connective segment)-(electron acceptor). In 1994, it was shown [BAT94] that there is an optimal combination of donor and acceptor strengths required to

maximize the nonlinearity for a given connective segment and beyond that point, increased donor-acceptor strength leads to a diminution of hyperpolarizability. More specifically, optical nonlinearity can be enhanced by maintaining good electron correlation in both the ground (i.e., neutral form) and excited (i.e., charge separated) state of the simple two-level model of nonlinearity. In practice, this situation has been achieved in chromophores that possess an amino donor and one of a variety of acceptors characterized by carbonyl-containing heterocyclic rings. In the attempt to improve optical nonlinearity, we must be careful not to push (red shift) the optical band edge too near the operating wavelength, which is a normal consequence of good electron correlation in extended π -conjugated systems. One way to keep the nonlinearity large while restricting the band edge to lower wavelengths is to replace the carbonyl acceptor of the ring with the related imino group. Thus, by: (1) modifying known high- β acceptors (thiobarbituric acids, 5-phenyl isoxazolones, etc.) as well as new acceptors developed at USC; and (2) choosing the appropriate conjugation length between the donor and acceptor pair, chromophores that are optically transparent at 980 nm can be synthesized.

Once chromophores with appropriately optimized hyperpolarizabilities and optical transparencies have been developed, they can then be incorporated into polymer lattices by novel synthesis and processing techniques. Such methods include preparation of optical quality films using processible precursor polymers, ordering of the chromophores within the polymer lattice by electric field poling near the glass transition temperature of the precursor polymers, and locking-in of poling-induced order by solid state chemical (crosslinking and condensation) reactions. These hardened polymeric materials typically exhibit large optical nonlinearities characterized by exceptional thermal stabilities, even for long term operation at elevated temperatures. These technologies will be employed in Phase II to develop an optimized polymer materials system for a prototype PSM display.

Table 1: EO Polymer Material Specifications

Material System Properties @ 980 nm (core/cladding)	PU-DR19/ Epoxylite (USC)	Stage I Technology Demonstration	Stage II 1st Generation Product	Stage III 2nd Generation Product
Development time frame	Today	Potentially Available Today	Would Like by 12/97	Wish List by 12/98
r_{33} (pm/V)	10-15	>15	>30	>100??
Planar waveguide optical loss of poled film (dB/cm)	<1	<1	<0.5	<0.1
Intrinsic unpoled absorption loss (dB/cm)	<0.2	<0.1	<0.1	<0.1
Δn (core-cladding) poled, TM	0.2	>0.1	>0.1	>0.1
r_{33} temp. stability (1000 hr to 90%)	85-110 C	>85 C	>120 C	>150 C
Core/Cladding conductivity ratio (at the poling temperature)	1/100	1/100	1/100	1/100
IR Photostability (1 MW/cm ²)	poor	1 yr	2 yr	50 yr
Visible photo-stability (480 nm)	Photo-bleaches	r_{33} stable in exposure to room lights for >1000 hrs.; no photobleaching in visible (uv photobleaching OK)		
Core/cladding integrated material system (bonding)	None	If available	Yes	Yes
Polymer solution stability for processing		Polymer must be stable for >24 hrs to be able to use a meniscus polymer coater		
Release layer between polymer and glass (flexible)	None	None	Yes	Yes

2. SUMMARY OF PHASE I RESULTS

2.1 PHASE I TECHNICAL OBJECTIVES

Phase I was comprised of three technical tasks, two of which were proposed and one of which was added after contract award. The goal of Task 1 was to investigate the feasibility of using imino groups as electron acceptor groups in known large- β chromophores as a means of inducing a blue shift in the absorption spectra without compromising the hyperpolarizability parameter. The goal of Task 2 was to incorporate these chromophores onto a polymer chain to form active electro-optical (EO) polymers through appropriate synthesis, processing, and electric E-field poling. The goal of Task 3 was to fabricate optical waveguides and characterize the optical loss and EO coefficient of these waveguide structures at 980 nm. The results of this work are presented in detail in the following section.

2.2 PHASE I TECHNICAL RESULTS

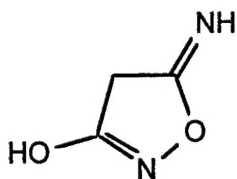
Task 1. Investigate the feasibility of replacing imino groups as electron acceptor groups in known large β chromophores as a means to induce a blue shift in the absorption spectra without compromising the hyperpolarizability parameter.

We explored six different methods of optimizing high- $\mu\beta$ chromophores for low absorption loss at 980 nm and high bulk nonlinearity. The Phase I work focused on second-order optical nonlinearities in dipolar chromophores of the general form (electron donor)-(π -bridge)-(electron acceptor). Two of the methods studied focused on improving the electron donor functional group; two focused on improving the π -bridge architecture; and two focused on improving the electron acceptor functional group. These methods, labeled a) through f), respectively, are discussed in some detail in the following sections.

a) Replace the carbonyl moiety in heterocyclic acceptors with the related imino moiety

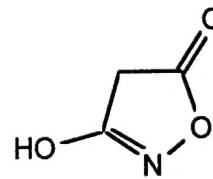
In the Phase I proposal, this was the method deemed most likely to blue shift the peak absorption wavelength while maintaining approximately the same EO coefficient. While the Phase I results indicated that this is indeed the case; at this time, the preparation of these materials remains problematic. As is common with high- $\mu\beta$ chromophores, obtaining ample quantities is hindered by low reaction yields. However, new methods of synthesizing such chromophores are constantly being developed and there is reason to believe that the yield problems associated with this reaction will be solved in the near future. For these reasons, this approach has been selected as a candidate for Phase II.

In Phase I, we endeavored to produce EO materials of low intrinsic loss at 980 nm by replacing the carbonyl functional group in the so-called high- β electron acceptors with the chemically-related imino functional group. The particular one we chose is shown in the figure at the top of the next page.



pyrazolone anil

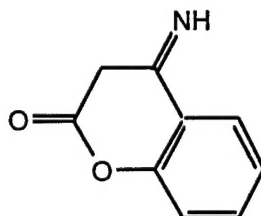
blue-shifting acceptor analog of



We prepared this acceptor and incorporated it into various chromophore architectures. Comparison of these chromophores with their carbonyl-containing counterparts showed that blue-shifting was indeed achieved while still maintaining a relatively high optical nonlinearity. Unfortunately, this achievement was offset by our inability to synthesize adequate amounts of these materials. Despite an exhaustive attempt, the key coupling step in the preparation of these chromophores remains unacceptably low.

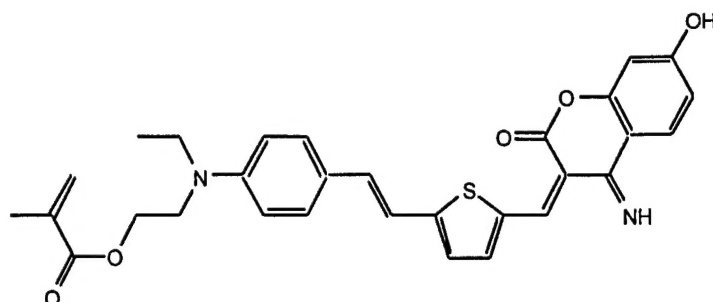
Work focused on developing a synthesis procedure for a promising imino-group-substituted EO polymer expected to have a significantly blue shifted absorption spectrum while maintaining a high nonlinear hyperpolarizability. The synthesis of this chromophore, designated iminopyrazolone, is accomplished by the coupling of essentially three key intermediates. The accepted method for producing this type of high- β EO chromophores (architecture characterized by donor-bridge-acceptor) involves the Knoevenagel condensation of an electron-rich aldehyde (donor-bridge) with an active methylene group (acceptor). Unfortunately this critical reaction occurs in low yield (the highest reported is 40%, with typical values around 20%), which wastes precious donor-bridge material. In Phase I, we made partial progress toward developing an alternative synthesis methodology to improve the overall yield of these chromophores, achieving yields for the key coupling step in the range of 80 to 98%.

Since we were able to demonstrate that this approach does indeed work, the idea was pursued further by carrying out similar studies on other imino-containing acceptors, such as the imino-coumarin shown below.



imino-coumarin

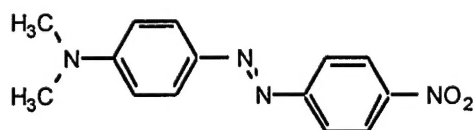
An attractive feature of this acceptor is that it is essentially the nucleus of the rhodamine family of laser dyes, and so should possess similar characteristics (chemical, thermal, photo- and oxidative stabilities) of the rhodamine dyes. We synthesized both the parent acceptor as well as the imino analog. Chromophores using these acceptors, such as the one shown at the top of the next page, were successfully prepared, and the problems associated with the original acceptor (pyrazolone anil) described above are not present in these new systems.



b) Replace the nitro acceptor in conventional chromophores with trivalent boron acceptors

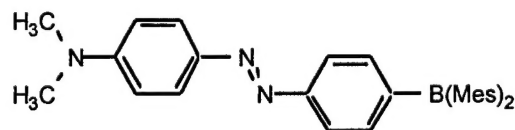
A second method for “engineering” low loss and high nonlinearity is with organoboranes. This is a new idea that was developed during the Phase I project. In all the cases studied, when compared to the nitro-acceptor analog, the boron-containing chromophores displayed a slightly larger nonlinearity while blue-shifting the absorption band. This chromophore has, therefore, been selected as a candidate for Phase II.

Organic trivalent boron compounds (called organoboranes) exhibit unusual properties arising from the electron deficiency of the boron atom. One such property is its ability to efficiently accept electron density and stabilize negative charge in intramolecular charge-transfer systems, thus potentially yielding high optical nonlinearities. In aromatic boron-ylide systems, it has been shown definitively that the negative charge is stabilized by and rests predominately on the electron deficient boron atom [RI81, BP86]. Furthermore, semi-empirical calculations using the ZINDO formalism carried out by Kanis, *et al.* [KRM91] and studies of organoborane-terminated chromophores by several groups [YTM90, LLC92, LLC91] have shown that trivalent boron is indeed an effective electron acceptor for electro-optical applications. Shown below is an example of a trivalent boron-containing chromophore analog of the well-known disperse red type:



$$\lambda_{\max} = 498 \text{ nm (CHCl}_3\text{)}$$

$$\beta_o = 40 \times 10^{-30} \text{ esu}$$

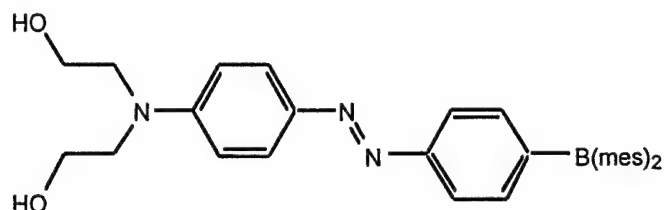


$$\lambda_{\max} = 446 \text{ nm (CH}_2\text{Cl}_2\text{)}$$

$$\beta_o = 72 \times 10^{-30} \text{ esu}$$

It can be seen from the figure above that a significant blue shift (52 nm) is observed, accompanied by a concomitant increase in static hyperpolarizability. The boron-containing chromophores possess a lower ground-state dipole moment than the corresponding nitro-containing chromophores and, thus, should not suffer from significant dipole-dipole interactions (to be discussed later) until very high chromophore loading densities are reached (typically well above practical values). These lower ground-state dipole moments may be compensated for by poling under a proportionately higher electric field during processing of these materials. Furthermore, these types of chromophores have been shown to be stable to air, insensitive to light, are thermally robust and are soluble in common organic solvents [DBG72].

We synthesized the boron analog (shown above) of disperse red, as well as many others, and confirmed the blue-shifting phenomenon in this class of materials. They appear to be excellent materials warranting further examination. In Phase II, we will continue the characterization of this class of materials, as well as the preparation of similar molecules that have substantially higher nonlinearities yet keep the absorption maxima shifted toward the blue end of the spectrum, relative to that of nitro analogs. Analogs of these chromophores will also be prepared to allow for incorporation into lattice-hardening protocols necessary to preserve EO activity. One such analogue is illustrated below.



c) Use of alkoxy donors in conjunction with high- β acceptors

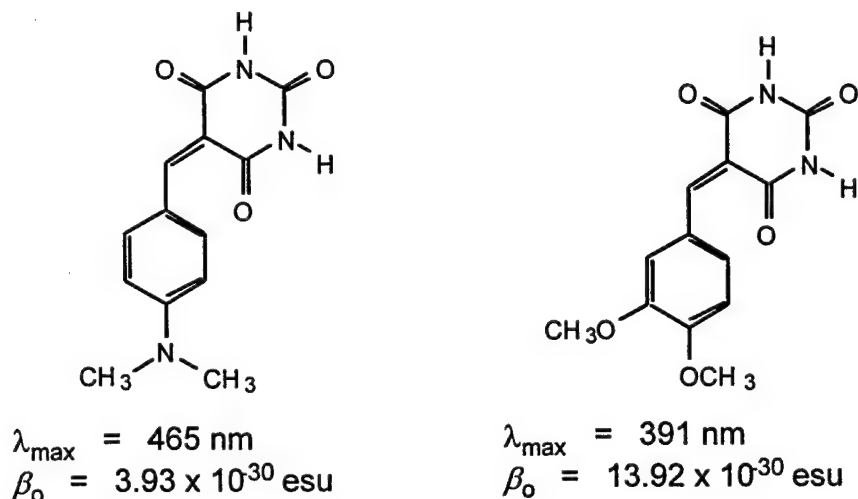
Use of alkoxy donors in conjunction with high- β acceptors is a new idea that was developed during the course of the Phase I project. It is known that the alkoxy donor will blue shift the λ_{max} of the chromophore. This is promising but largely unexplored territory. We, therefore, judge the probability of success with this approach is significantly lower than that of the others; and, hence, we have not selected it for further study in the Phase II program.

Alkoxy donors have traditionally been regarded as inferior to the dialkylamino donors in second-order nonlinear optical chromophores. This convention evolved from observations of chromophores containing traditional electron acceptors (such as nitro, cyano, sulfonyl, di- and tricyanovinyl). Chromophores containing alkoxy donors generally possess only 50-60% of the optical nonlinearity (β_0) of the dialkylamino analog. Even though alkoxy-donor chromophores possess an absorption maximum blue-shifted by as much as 75 nm relative to the dialkylamino-donor counterparts, the traditional belief is that this blue-shift is not worth the loss in optical nonlinearity. It is not surprising then that with the discovery of high- β acceptors, the design of practical high- β chromophores have focused almost exclusively on dialkylamino donors. Chromophores incorporating these new acceptors and alkoxy donors have been virtually ignored (to our knowledge, only *two* chromophores of this type have been studied and no results have yet been published). The increase in optical nonlinearities (commonly in excess of an order of magnitude) afforded by the high- β acceptors should *considerably more than compensate* for the loss in optical nonlinearity encountered when using an alkoxy donor. Hence, materials incorporating alkoxy-donor and high- β acceptor terminated chromophores could arguably be expected to possess device-viable optical nonlinearities (due to the acceptor) as well as acceptable intrinsic optical losses (due to the donor) in the near-infrared and infrared wavelength operating region. This idea was studied for flaws in Phase I and successfully withstood close scrutiny. However, due to the availability of more promising approaches, we do not plan to actively pursue this approach as a first priority in Phase II.

d) Use of 3,4-dialkoxyphenyl-based systems

One chromophore with a dialkoxyphenyl donor has been reported in the literature which purportedly exhibits a significant increase in nonlinearity over the dialkylamino donor and is accompanied with a 75-nm blue shift. We were unable to corroborate this result and this class of chromophores will not be pursued further.

It has recently been reported [SWC95] that 3,4-dimethoxybenzylidenebarbituric acid (below, right) possesses a significantly larger first hyperpolarizability over the 4-dimethylamino analog (below, left). This increase is accompanied by a large blue shift in the optical absorption spectrum of these chromophores.

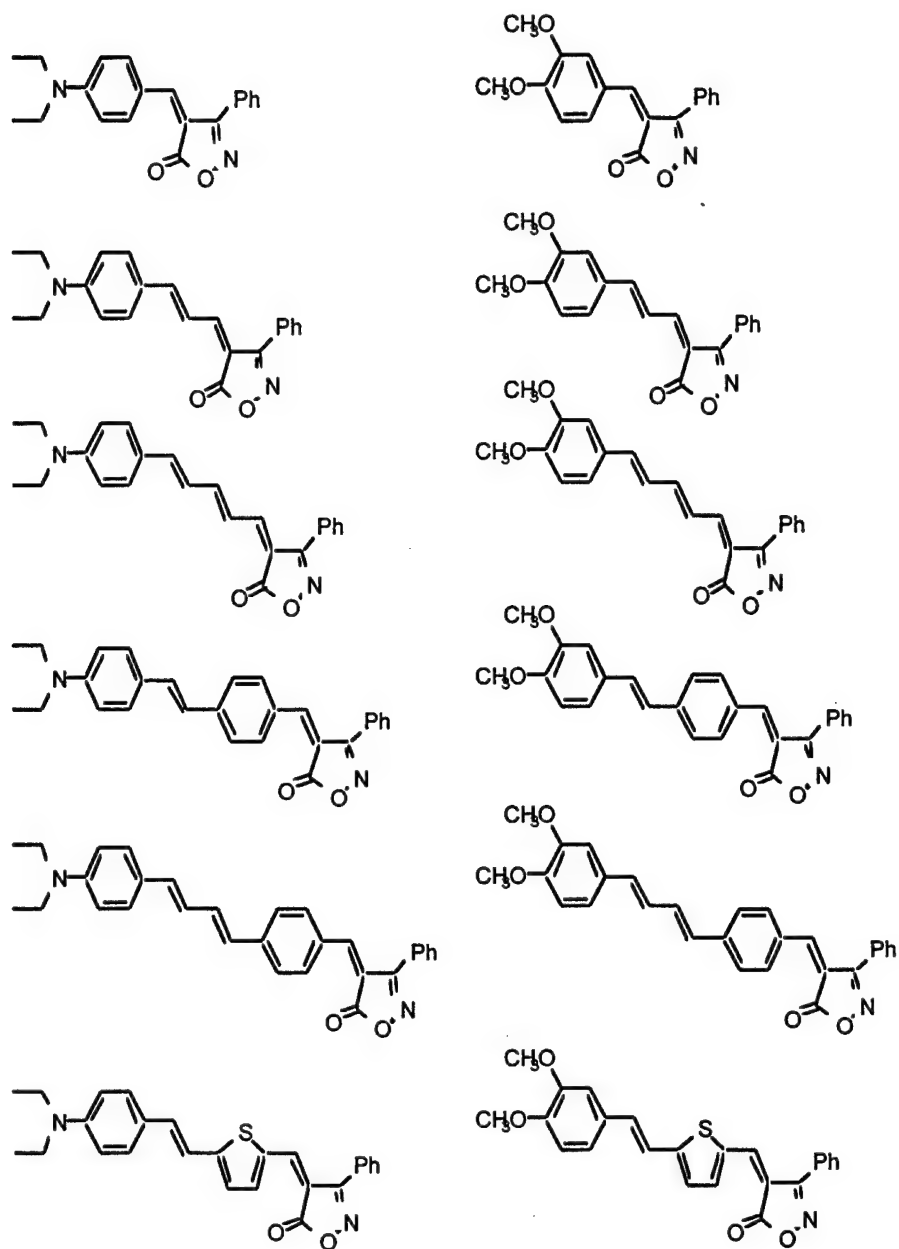


In Phase I, we explored the generality of this phenomenon by evaluating the optical and secondary characteristics (solubility, photochemical, oxidative, electrochemical, and thermal stability, etc.) of the series of chromophores shown at the top of the next page. The results were inconclusive, casting doubt on the viability of this approach for our purposes.

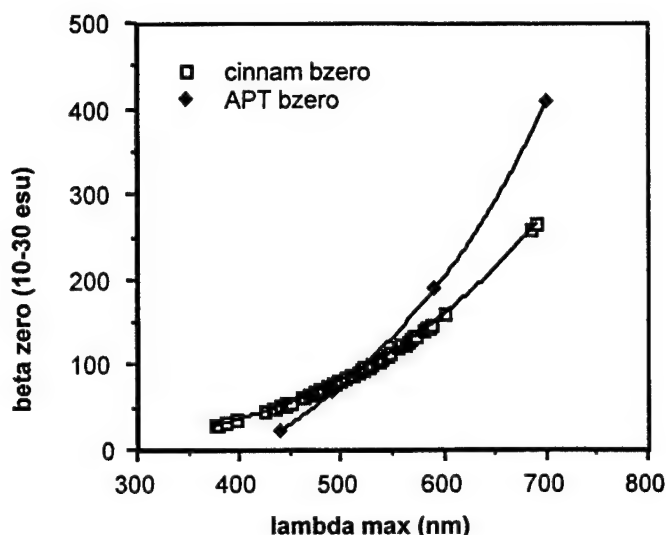
e) Nonlinearity-transparency tradeoff involving judicious choice of electron acceptor and/or conjugation bridge

In Phase I, we synthesized a large number of different chromophores with combinations of donor and acceptor groups with the intent of "engineering" a chromophore that gives an appropriate compromise between nonlinearity and transparency. We evaluated $\mu\beta$ and λ_{\max} , the peak absorption wavelength, as the figures of merit, and constructed a universal plot that helps in evaluating the tradeoff between loss and EO activity. The data show that a universal plot of β_0 vs. λ_{\max} can be constructed and fitted to theory for a specific bridge structure, and that this transparency tradeoff is different for different bridge structures. Moreover, the data show that for a given λ_{\max} , the chromophore structure *can* be optimized to give the largest nonlinearity.

To demonstrate this method, we developed over 80 new electron acceptors which have been shown to produce chromophores that span several orders of magnitude in optical nonlinearity



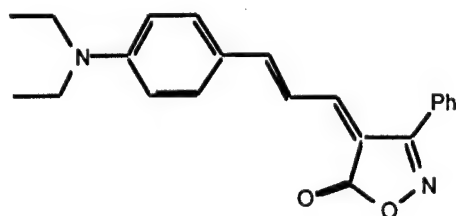
and encompass the entire visible optical spectrum. Thus, we are now in position to choose one or several of these acceptors in conjunction with an appropriate donor and π -bridge (conjugated connective segment of an appropriate length and architecture) to produce chromophores that will be translated into low-loss materials with adequate-to-excellent nonlinearities for device applications. In essence, the strategy is to produce viable materials for this low-loss 980-nm application by careful selection of conventional and new molecular building blocks. At the top of the next page is a plot showing the nonlinearity/transparency relationship for these acceptors attached to two different bridge systems, 4-(donor)-cinnamylidene and 1-(4-donor)-phenylene-2-thien-5-ylidene. Note that chromophore design can strongly affect the tradeoff between nonlinearity and transparency. This plot will be very valuable in Phase II for selecting for development those chromophore materials systems most likely to be suitable for our application.



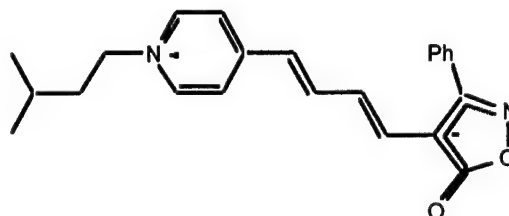
f) Use of negative-solvatochromic chromophores

Negative-solvatochromic chromophores are largely charge-separated in the ground state. Chromophores of this type yield negative $\mu\beta$ values and this effect allows for blue shifting of the λ_{max} relative to that of a similar "conventional" chromophore. In Phase I, we synthesized a model system that is composed of two molecules of similar donor and acceptors with the same conjugation length. The conventional chromophore (which is ground-state charge-neutral dominant) displayed the familiar red-shifting upon increasing the host matrix polarity. The negative-solvatochromic counterpart (which is ground-state charge-separated dominant) displayed a remarkable blue-shifts (>50 nm) upon increasing the host polarity. This chromophore has been selected as a candidate for Phase II.

Negative-solvatochromic chromophores yield negative hyperpolarizabilities, since polarization occurs from "acceptor" to "donor" for conventional chromophores. The model system we synthesized during Phase I is composed of two molecules of similar donor and acceptor and of the same conjugation length, as shown below.



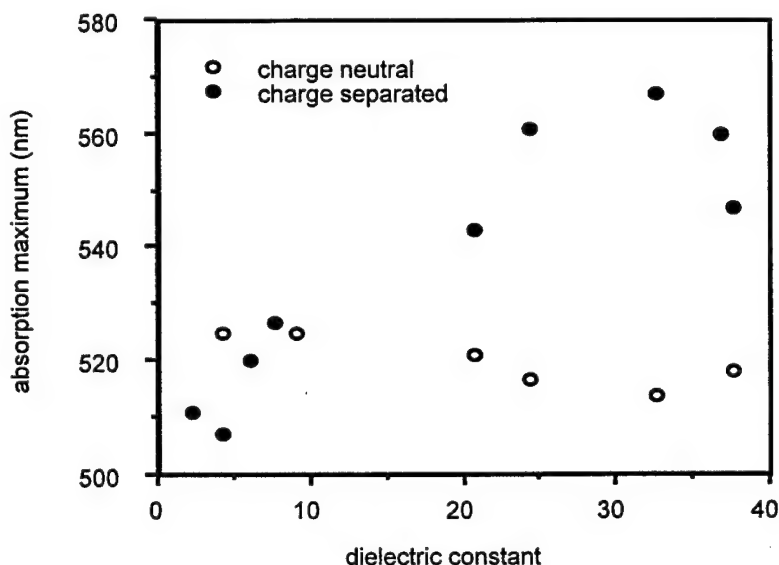
$$\mu\beta = 1202 \times 10^{-48} \text{ esu at } 1.907 \text{ } \mu\text{m}$$



$$\mu\beta = -3200 \times 10^{-48} \text{ esu at } 1.907 \text{ } \mu\text{m}$$

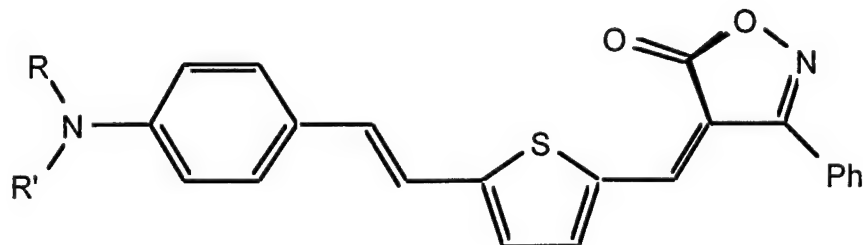
The conventional chromophore, which is ground-state neutral dominant, displays the familiar red-shifting upon increasing the host matrix polarity. The negative solvatochromic counterpart, which is ground-state charge-separated dominant, has the same terminal functionalities but their donor/acceptor roles are reversed with respect to the conventional chromophore and the same conjugation length. As can be seen in the figure below, this charge-separated chromophore has a substantially larger nonlinearity. Furthermore, its solvatochromic behavior, shown below in comparison with the charge-neutral counterpart in solvents of varying polarities, indicates that a significant blue-shifting is observed (by as much as 53 nm).

In addition to the chromophore shown above on the previous page, we synthesized several others; all show similar behavior. Our observations have since been substantiated by several groups, both theoretically [BSP95] and experimentally [MLM94]. We plan to exploit this class of chromophores in Phase II to demonstrate a new class of NLO polymers that have exceptional optical nonlinearities and low optical loss at 980 nm.

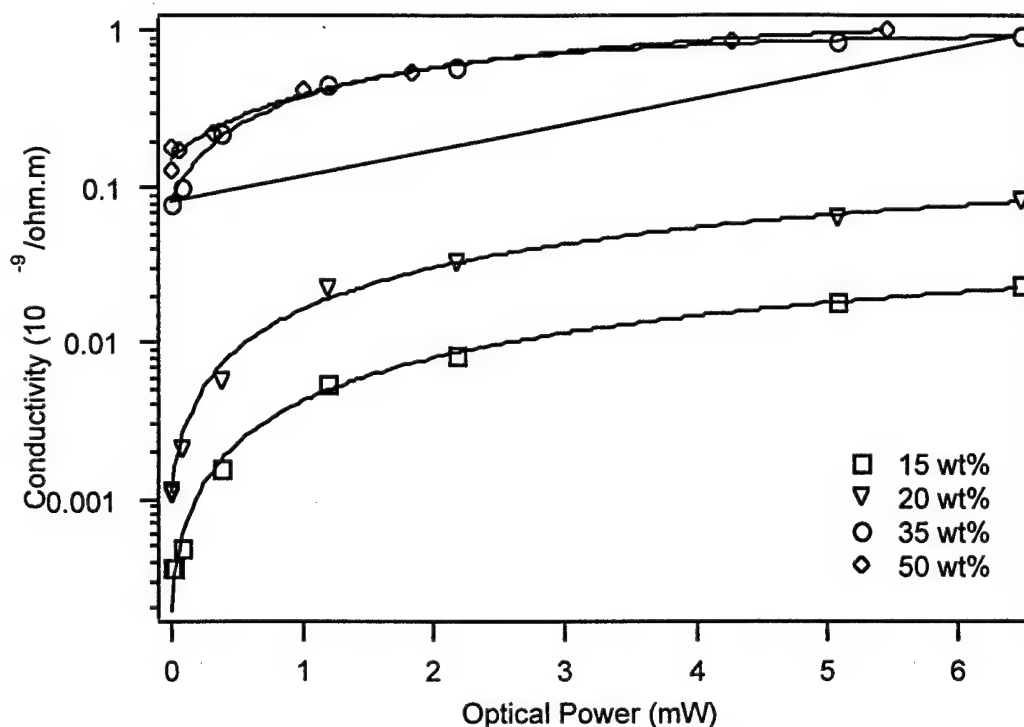


Task 2. Incorporate these chromophores onto a polymer chain to form active electro-optical polymers through appropriate synthesis, processing, and electric field poling.

One particularly promising chromophore was selected and focused upon in Task 2. This candidate is of type d) and denoted ISX. Its structure is shown below:



The chromophore has a $\mu\beta_0$ three times that of disperse red-type chromophores and more than an order of magnitude greater than disperse red types at 980 nm. We examined this chromophore in a variety of polymer hosts (PMMA, polycarbonate, and poly(1,4-(2-benzoyl)phenylene). We also made a high- $\mu\beta$ analog of the well-known PU-DR19 polymer system previously developed at USC, denoted PU-ISX(N), where N is the weight percent of chromophore and PU stands for polyurethane. Similar thermostabilities were achieved, but the magnitude of the bulk optical nonlinearity was smaller than expected. Two major causes for this behavior were identified. First, polymer systems incorporating the ISX chromophore were found to have pronounced photoconductivity, as shown in the figure below. One solution to this problem for a typical EO

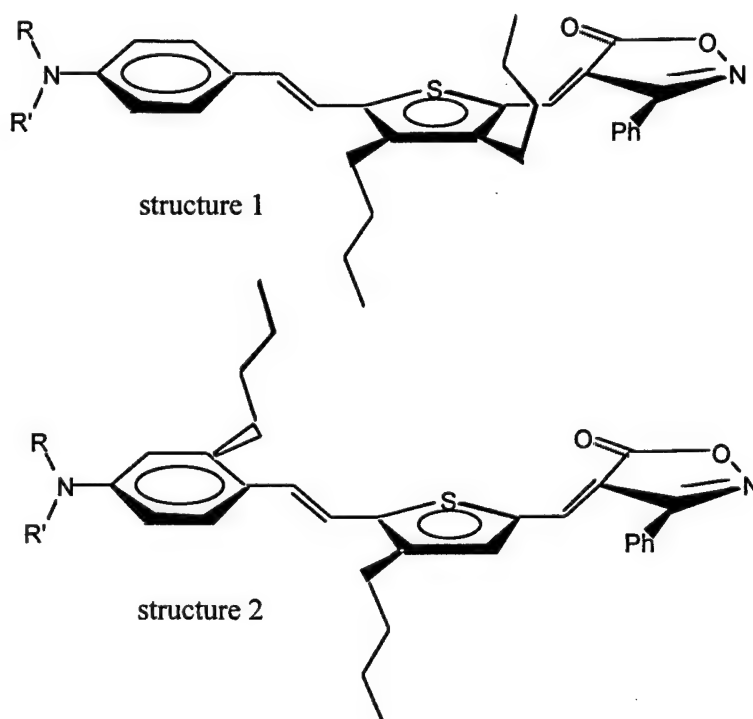


device is to pole the system in the absence of light. It remains to be seen if this phenomenon will affect our display application, since a significant amount of visible light is generated in the display and may change the photoconductivity and resultant observed nonlinearity of the active layer. On going work at USC is reinvestigating the guest-host and PU-ISX(N) systems by comparing the performance of the materials processed in the presence and absence of room light.

The second cause for the low EO coefficients is the observation of strong dipole-dipole interactions in these systems. We have observed that centrosymmetric aggregation occurs at moderate loading densities for this chromophore, and this tendency has been successfully modeled by quantitative London theory. These observations have given us new insights on how to optimize or at least affect poling procedures for these high- $\mu\beta$ chromophores. Under separate funding, USC is presently exploring two approaches to overcome these strong dipole-dipole interactions. The first method is to derivatize the chromophores so that they physically cannot form centrosymmetric aggregates (see figure on next page) using a so-called "bumper car"

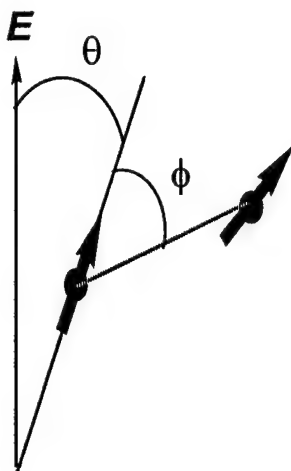
approach. The chromophores are not allowed to approach each other so closely that, by dipole-dipole interactions, an energetically favorable centrosymmetric structure is formed. This allows them to maintain a high density of chromophores that may be poled efficiently into the required noncentrosymmetric orientation.

The second method is to employ host polymer matrices (e.g., poly(dimethylacrylamide) types) that efficiently solvate the chromophores, and so "shield" each chromophore from the local effects produced from a neighboring chromophore. USC, under a separate but related activity, reports that they have successfully synthesized a series of eight copolyesters incorporating the ISX chromophore in regular intervals of loading densities and are currently characterizing these polymers using NMR, GPC, DSC and TGA. They subsequently plan to determine their nonlinear optical properties.



Having identified an unexpected source of difficulty in realizing the full macroscopic optical nonlinearity expected from improved hyperpolarizability chromophores as arising from chromophore-chromophore electrostatic interactions, we made good progress in Phase I in determining the cause at a more fundamental level. In principle, three factors can influence the resulting order of chromophores placed in an external electric field: (1) chromophore-poling field electrostatic interactions which attempts to induced acentric order; (2) chromophore-chromophore electrostatic interactions which attempt to induced centric order or centric crystallization; and (3) entropic effects or thermal collision effects which attempts to induce random order. Traditional theoretical treatments have neglected the consideration of chromophore-chromophore electrostatic interactions. While such an approximation is acceptable for analyzing the behavior of chromophores characterized by modest polarizability, it is not

acceptable for high-number-density chromophores, especially those characterized by large dipole moments, hyperpolarizabilities, or ionization potentials. USC undertook to re-examine this problem from the standpoint of treating all three effects with minimum approximation. The treatment of two interacting chromophores in an electric field is non-trivial and in general requires consideration of three coordinate systems and three rotational matrices that inter-relate them. The figure below illustrates the reduction of the problem to its simplest form involving two simple rotation matrices relating the three coordinate systems.

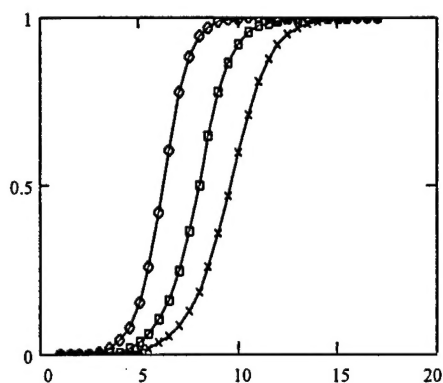


While USC generally treats the problem of computing electrostatic interactions between arbitrarily shaped chromophores from basic principles and add molecular dynamics to the numerical simulations to gain insight into non-transient interaction or crystallization effects, that was not required here. Instead, the problem of chromophore-chromophore interactions was re-investigated, avoiding many of the approximations originally made by London. Handled properly [Dal96], it is possible to obtain an analytical expression explicitly showing that a maximum is predicted in the variation of EO coefficient versus chromophore loading and the attenuation of optical nonlinearity with increasing chromophore-chromophore interactions at high loading. Hence, even at the level of approximation (i.e., spherically shaped chromophores and negligible effects due to chromophore molecular dynamics), it is clear that the commonly used figure-of-merit expression, $\mu\beta/MW$, where MW is the molecular weight of the given chromophore, is not appropriate for high polarizability chromophores.

The figure below shows the attenuation of chromophore order with decreasing average separation of spherical chromophores (i.e., with increasing chromophore loading). As the chromophore electrostatic interactions are increased by increasing dipole moment, polarizability, or ionization potential, the attenuation onsets at larger average separation distances (i.e., lower loading). Note the dramatic dependence of order upon chromophore separation; once order begins to be lost, it is lost very quickly over a small range of change in average separation.

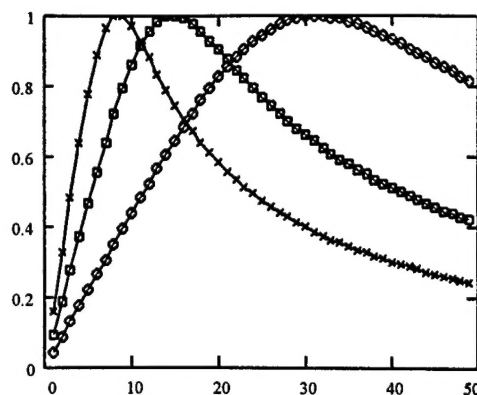
In the next figure, we show the translation of these theoretical results into more experimentally relevant plots of the variation of electro-optic coefficient with chromophore loading. Note that with increasing chromophore electrostatic interactions, the maxima in the curves shift to lower chromophore loading and the curves become sharper.

Order Attenuation Factor Versus Chromophore Separation



Chromophore Separation, R (angstroms)

Normalized Electro-Optic Coefficient Versus Chromophore Number Density

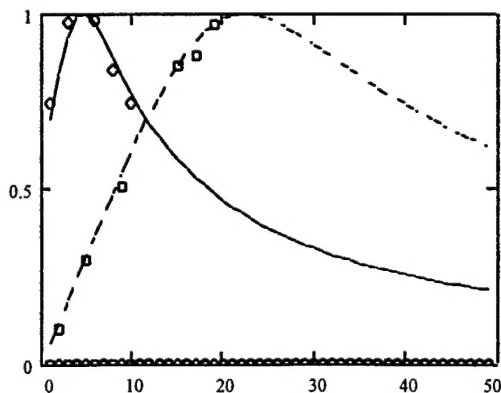


Chromophore Number Density ($10^{20}/\text{cm}^3$)

Calculated attenuation of acentric order and variation of normalized EO coefficient versus chromophore loading are shown for increasing chromophore electrostatic interaction (crosses > boxes > diamonds).

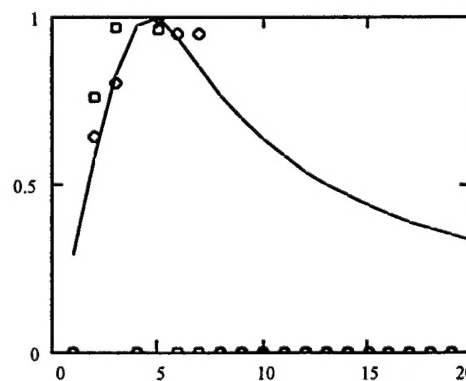
Below, we show the comparison of the results of these theoretical calculations with typical experimental measurements. Note that detailed experimental investigations were carried out for disperse red, ISX, and other chromophores either physically incorporated into poly(methyl methacrylate) (denoted PMMA); poly(carbonate) (denoted PC); or poly(p-phenylene) (denoted PP) polymers to form composites, or covalently coupled to PMMA or PU polymer backbones. In all cases, maxima in the electro-optic coefficient versus chromophore loading curves are observed, consistent with theory. For all samples, excellent agreement was obtained between theory and experiment using experimentally determined values of chromophore dipole moment,

Normalized Electro-Optic Coefficient Versus Chromophore Number Density



Chromophore Number Density ($10^{20}/\text{cm}^3$)

Normalized Electro-Optic Coefficient Versus Chromophore Number Density



Chromophore Number Density ($10^{20}/\text{cm}^3$)

Comparison of theory and experiment for DR(left, boxes), ISX (left, diamonds) and TCI (right, boxes and diamonds) chromophores.

polarizability, ionization potential (as determined by photoelectron spectroscopy), and dielectric data. It was found that for the disperse red or azobenzene chromophore, excellent simulation of experimental data could be achieved using the approximation of spherically shaped chromophores. At first this may seem puzzling until it is realized that the azobenzene chromophore can undergo photo-induced trans-cis-trans isomerization leading to an effective approximately spherical shape it may be quite reasonable. For other chromophores, the reconciliation of data required that their prolate ellipsoidal shapes be taken into account.

The excellent simulation of the data for the disperse red chromophore quantitatively explains the deviation from linearity of plots of electro-optic coefficient versus chromophore loading observed but not previously explained by other researchers. Note that Katz and coworkers at AT&T [KSW90] found that they could not quantitatively explain the deviation which they observed employing an equilibrium model taking into account formation of crystalline aggregates. The theoretical and experimental results of the USC group for the disperse red chromophore also illustrates why the nonlinear optical materials community was seduced into advancing the use of the $\mu\beta/\text{MW}$ figure-of-merit. No significant chromophore-chromophore interaction effects are observed for the disperse red chromophore. On the other hand, the severity of the problem for high- $\mu\beta$ chromophores is readily apparent from a consideration of the above observations.

Moreover, these results suggests a straightforward solution to the problem encountered for the prolate-ellipsoidal high-polarizability chromophores. According the to theoretical model, simple derivatization of the chromophores to inhibit close approach along the minor axes of the prolate ellipsoid should result in dramatically improved optical nonlinearity; and, indeed, it was experimentally observed by USC that simple derivatization of the ISX and TCI chromophores leads to doubling of the observed macroscopic optical nonlinearity. Theory predicts also that optimum results will be obtained for spherically-shape chromophores.

Task 3. Fabricate optical waveguides and characterize the optical loss and electro-optic coefficient of these waveguide structures at 980 nm.

Subsequent to the Phase I award, a third task was added to the work plan. The waveguide loss of several high- $\mu\beta$ chromophores were measured in a poled guest-host polymer material system. Intrinsic measurements of the absorption spectrum at 980 nm indicates that the λ_{max} can be red shifted to longer than 550 nm (as in the case of isoxazolone) before the tail of the chromophore absorption starts to affect transmission losses at 980 nm. This is a very significant results, since it expands the parameter space in which the nonlinearity/transparency tradeoff can be optimized. Continuing to optimize the chromophore for low absorption loss will require investigating the requirements for preventing crystallization/aggregation of the chromophores. This work will be included in the Phase II work plan.

3. CONCLUSIONS AND RECOMMENDATIONS

The goal of Phase I was to develop high- $\mu\beta$ chromophores with low absorption loss and high bulk EO nonlinearity at 980 nm. Six different methods of "engineering" such material were explored. Four showed sufficient promise to warrant further consideration in Phase II. Phase I also attempted to incorporate one particularly promising chromophore into a polymer host but less-than-expected bulk nonlinearities were encountered due to what was ultimately determined to be centrosymmetric crystallization. This phenomenon was successfully modeled with London theory and a quantitative comparison between theory and experiments performed. From the quality of these results Phase II solutions to the observed problem can be postulated with good confidence. Lastly, the Phase I work plan was expanded to include measurements of waveguide loss of several high- $\mu\beta$ chromophores in a poled guest-host polymer material system. Intrinsic measurements of the absorption spectrum at 980 nm indicates that the λ_{max} can be red shifted to longer than 550 nm before the tail of the chromophore absorption starts to affect transmission losses at 980 nm. This is a particularly significant result; since it expands the parameter space in which the nonlinearity/transparency tradeoff can be optimized during Phase II. Based on these excellent results, the feasibility of developing a protocol for systematically designing blue-shifted chromophores with high bulk nonlinearities has been established. Moreover, by exploring not one, but several promising materials systems, a solid theoretical and experimental foundation for the Phase II work has been laid, greatly reducing the technical and commercial risk. Based on these exceptional results, we strongly recommend continued development of this highly promising technology.

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